Polymerization of acrylamide initiated with Ce(IV)- and KMnO₄-mercaptosuccinic acid redox systems in acid-aqueous medium

C. Özeroglu*, S. Sezgin

Department of Chemistry, Faculty of Engineering, Istanbul University, 34320 Avcilar Istanbul, Turkey

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Abstract. By using mercaptosuccinic acid-cerium(IV) sulfate and mercaptosuccinic acid-KMnO₄ redox systems in acid aqueous medium, the polymerization of acrylamide monomer was performed at room temperatures. Water soluble acrylamide polymers which contain mercaptosuccinic acid end-groups were synthesized. The dependence of polymerization yield and the molecular weight of polymer on the initiator concentration (n_{MSA} = n_{Ce(IV)} ) at different acid concentrations, polymerization time, temperature, and concentration of sulfuric acid was investigated. The decrease in the initiator concentration resulted in an increase in the molecular weight but a decrease in the yield. The increase of reaction temperature from 20 to 60°C resulted in an increase in the molecular weights and slight decrease of the yield of polymer. Cerium and manganese ions are reduced to Ce(III) and Mn(II) ions respectively in polymerization reaction. The existence of Ce(III) ion bound to polymer was investigated by UV-visible spectrometry and fluorescence measurements. The amount of Mn(II) which is incorporated to the polymer was determined.

Keywords: polymer synthesis, molecular engineering, mercaptosuccinic acid, cerium(IV) sulfate, redox polymerization, acrylamide

1. Introduction

KMnO₄ and ceric salts-(organic) reducing agent systems in acid-aqueous medium were used for polymerization of vinyl monomers. These methods have also been used for the preparation of graft copolymers of vinyl monomers such as acrylonitrile, methylmethacrylate, acrylic acid or acrylamide [1–15]. In previous studies, water soluble polymers containing amine, hydroxyl, carboxyl, dicarboxylic or amino tri(methylene phosphonic acid) end groups were synthesized by using redox initiator systems [16–23]. The initiator system, especially using mercaptosuccinic acid was used firstly in this study. Unlike other reducing agents used in most previous studies, mercaptosuccinic acid contains S–H group. The formation of –S’ radicals are more probable at low temperatures, because of low bonding energy of S–H bond. This gives advantages us to save energy in polymerization process and to obtain polymer with low degree of branching. Moreover if mercaptosuccinic acid is used as a reducing agent, polyacrylamide bearing mercaptosuccinic acid end groups is synthesized. Because of the presence of this functional group in the polymer, it may also find some practical applications in various industries. In the present communication, the polymerization of acrylamide monomer initiated by cerium(IV) sulfate-mercaptosuccinic acid and potassium permanganate-mercaptosuccinic acid redox systems was investigated at room temperatures. The effects of initiator concentration (n_{MSA} = n_{Ce(V)} ), polymer-
ization time, temperature, the concentration of sulfuric acid on the polymerization yields and the molecular weights of polymers were investigated. Water soluble polyacrylamides containing mercapto succinic acid end groups were synthesized. Such water soluble polymers prepared with Ce(IV)-organic reducing agent redox system containing amino, hydroxyl, carboxylic and thiol functional groups or end groups seem to be potential sources for the construction of high molecular weight polymers that can be destroyed under physiological conditions due to weakly bound structures occurring in the polymer and to have potential for the preconcentration and separation of some trace elements [24–28].

2. Experimental

Mercaptosuccinic acid (Merck), acrylamide (Merck), cerium(IV) sulfate (Merck) and sulfuric acid (Merck) were used without further treatment. Ce(IV) sulfate, mercaptosuccinic acid and acrylamide are denoted as Ce(IV), MSA and AAm respectively. Polymerizations were carried out in a round-bottomed flask equipped with a stirrer by adding the calculated amount of Ce(IV) salt or KMnO₄ solution to aqueous solution of acrylamide monomer and mercaptosuccinic acid. The oxidants (cerium(IV) sulfate and potassium permanganate) were dissolved in the calculated amount of sulfuric acid solution. The solution volume containing oxidant was kept constant at 20 ml. The total volume of polymerization solution was 100 ml. It was reported that H₂SO₄ was used to increase the solubility of the oxidant and to prevent the hydrolysis of the oxidant. Moreover, the redox reaction between mercaptosuccinic acid and Ce(IV) or KMnO₄ salt takes place in acetic medium [1–22, 30–34]. After polymerization was completed, the solution was poured into an excess of acetone to precipitate the raw polymer. In the precipitation of polymers in acetone, volume ratios of acetone to polymer solution were exactly 7/1. The weight of isolated polymer was determined by direct weighting of polyacrylamide dried in air and the yield % was calculated by using Equation (1).

\[
\text{Yield} \, [%] = \frac{\text{weight of isolated polymer} \, [\text{g}]}{\text{weight of monomer} \, [\text{g}]} \times 100 \, (1)
\]

In polymerization reaction, the effects of the initiator concentration (\(C_{\text{Ce(IV)}} = 1.4 \times 10^{-3}, \ 2.8 \times 10^{-3}, \ 7 \times 10^{-3}, \ 14 \times 10^{-3} \) and \(20\times 10^{-3}\) mol/l) at different acid concentrations, the temperature (\(T = 20, \ 30, \ 40, \ 50\) and \(60°C\)), polymerization time (\(t = 5, \ 10, \ 30\) and \(60\) minutes) and the concentration of sulfuric acid (\(\text{CH}_2\text{SO}_4 = 0.05, \ 0.10, \ 0.20\) and \(0.40\) mol/l) on the yield and molecular weight were examined. The \(n_{\text{Ce(IV)}}/n_{\text{MSA}}\) ratio was kept constant at 1. It seems from previous investigations, that the formation of radicals on carboxyl groups may be possible [2, 33]. However, the probability of radical formation on carboxyl groups may appear less than that of other radical formation reactions given in Figure 1, due to the formation of acid (proton) influence. It was also described that the redox reactions in the use of thioglycolic acid and 3-mercap-

![Figure 1. Radical formation reactions occurring between mercaptosuccinic acid and Ce(IV) ions](image-url)
topropionic acid as reducing agents in the redox systems occur at lower temperature, due to low bonding energy of S–H bond [30, 34]. The radical generation is believed to occur by one electron transfer from mercaptosuccinic acid to Ce(IV) according to the reactions given in Figure 1 as reported in the literature [22, 30, 34]. Because of low S–H bonding energy, the formation of free radicals in reaction I in Figure 1 is more likely than other reactions to initiate polymerization of acrylamide and oxidative termination of polymer radicals is also possible by ceric ions [2, 22, 30, 33–36]. For this reason, in the polymerization reaction, water soluble polyacrylamides having more probable structures given below in Figure 2 have been obtained.

Infrared measurements were carried out with ATI Unicam (Mattson 1000) FT-IR spectrometer and the spectra of polymers were determined by KBr disk method. For this purpose, pallets of about 300 mg KBr powder containing finely grained powder of MSA, AAm or PAAm sample(7–8 mg) were made. The FT-IR spectra of MSA, AAm and PAAm synthesized using MSA-Ce(IV) redox system were recorded by ATI Unicam (Mattson 1000) FT-IR spectrometer.

For determination of the viscosity average molecular weight ($M_v$), the flow time of dilute solution of polyacrylamide with 0.5 g/dl and that of water (the average value of flow times for three measurements was 163±0.2 s for water at 30°C) was measured by an Ubbelohde-level viscometer at 30°C. The intrinsic viscosities ($\eta_I$) of polymer solutions were calculated by using Equation (2) [29–30].

$$\eta_I = \frac{\eta_{sp} + 3\ln(\eta_I)}{4C}$$

(2)

The relative ($\eta_r$) and specific ($\eta_{sp}$) viscosities were calculated using Equations (3) and (4).

$$\eta_r = \frac{t}{t_0}; \quad \eta_{sp} = \frac{t-t_0}{t_0} = \eta_r - 1$$

(3), (4)

to and t are the flow times of water and polymer solution of defined volume in Ubbelohde capillary viscometer.

In standard measurements, the solution viscosity is measured in at least three different concentrations and triplicates for extrapolation of the Huggins or Kraemer plots to infinite dilution. However, this method is quite laborious and time consuming. The molecular weights of polymers were determined by the Mark-Houwink equation (5).

$$\ln \eta = K M_v^\alpha$$

(5)

Where $K$ and $\alpha$ are constants which are dependent on the solvent, type of polymer and the temperature of system. For polyacrylamide aqueous solution at 30°C, the values of $K$ and $\alpha$ are 6.88·10$^{-4}$ and 0.66 respectively.

The UV measurements (200–1000 nm) were done using a JASCO V-530 UV/VIS spectrometer equipped with a temperature control attachment.

For fluorescence measurement, PTI QM-4/2003 spectrofluorimeter was used to establish the presence of Ce(III) in the polymer. 75 watt xenon lamp was operated at an excitation wavelength of 260 nm and a slit width of 1 nm An Analytik Jena Vario 6 AAS, flame atomic absorption spectrometer was used for determining Mn(II) in polymers. Manganese hollow cathode lamps were operated at a wavelength of 297.5 nm and a slit width of 0.2 nm.

3. Result and discussion

In the polymerization of acrylamide initiated by Ce(IV)- mercaptosuccinic acid or KMnO$_4$-mercaptosuccinic acid in acid-aqueous medium, the formation radicals of –S· is energetically most favorable due to low S–H bonding energy. Therefore the polymerization of acrylamide initiated with Ce(IV)-organic reducing agents such as polyamino, amino and carboxylic acids [17–22] requires higher energy, longer time and lower acid concentration.
than that initiated with Ce(IV)-organic reducing agents containing thiol groups.

The effect of initiator concentration at different acid concentrations (\(CH_2SO_4 = 0.05, 0.10\) and 0.20 mol/l) on the molecular weight of polymer and the yield are shown in Figure 3 and 4 respectively. The increase in the initiator concentration at a constant monomer concentration of 0.7 mol/l resulted in a decrease in molecular weight (Figure 3) but an increase in the yield (Figure 4) of polymer which contains mercaptosuccinic acid end-groups.

The increase of the temperature in the polymerization reaction resulted in an increase in the molecular weight of polymer and slight decrease in the yield of polymer (Figure 5). This unexpected result must be because of the side reactions of the primary radicals generated from mercaptosuccinic acid. Those side reactions might be recombination of the initiating primary radicals or any other radical addition to the amide carboxyl etc. Similar unusual behavior has been reported by Lozinsky et al. [32] in the polymerization of polyacrylamide initiated with tertiary amine-persulfate redox couple.

The dependence of the yield and molecular weight of polymer on the acid concentration at different

![Figure 3](image3.png)

**Figure 3.** The effect of the initiator concentration on the molecular weight of polymer synthesized by using mercaptosuccinic acid-Ce(IV) redox system at different acid concentrations. \(C_{H_2SO_4} = 0.05(•), 0.1(■)\) and 0.2(Δ). \(C_{AAm} = 0.7\) mol/l; \(T = 30°C; t = 10\) min; \(n_{Ce(IV)} = n_{MSA}\)

![Figure 4](image4.png)

**Figure 4.** The dependence of polymerization yield on the initiator concentration at different acid concentrations. \(C_{H_2SO_4} = 0.05(•), 0.1(■)\) and 0.2(Δ). \(C_{AAm} = 0.7\) mol/l; \(T = 30°C; t = 10\) min; \(n_{Ce(IV)} = n_{MSA}\)

![Figure 5](image5.png)

**Figure 5.** The effect of the temperature on the yield and molecular weight of polymer. \(C_{AAm} = 0.7\) mol/l; \(C_{Ce(IV)} = 7·10^{-3}\) mol/l; \(n_{Ce(IV)} = n_{MSA}; C_{H_2SO_4} = 0.05\) mol/l; \(t = 10\) min

<table>
<thead>
<tr>
<th>(C_{Ce(IV)}10^3) [mol/l]</th>
<th>(C_{H_2SO_4}) [mol/l]</th>
<th>Polymerization time [min]</th>
<th>Yield [%]</th>
<th>(M_v) [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>0.05</td>
<td>10</td>
<td>62.0</td>
<td>9 400</td>
</tr>
<tr>
<td>7.0</td>
<td>0.10</td>
<td>10</td>
<td>57.9</td>
<td>5 500</td>
</tr>
<tr>
<td>7.0</td>
<td>0.20</td>
<td>10</td>
<td>40.7</td>
<td>4 300</td>
</tr>
<tr>
<td>7.0</td>
<td>0.40</td>
<td>10</td>
<td>66.6</td>
<td>6 430</td>
</tr>
<tr>
<td>2.8</td>
<td>0.05</td>
<td>10</td>
<td>21.1</td>
<td>11 350</td>
</tr>
<tr>
<td>2.8</td>
<td>0.10</td>
<td>10</td>
<td>32.1</td>
<td>8 900</td>
</tr>
<tr>
<td>2.8</td>
<td>0.20</td>
<td>10</td>
<td>37.8</td>
<td>10 500</td>
</tr>
<tr>
<td>2.8</td>
<td>0.40</td>
<td>10</td>
<td>52.9</td>
<td>17 600</td>
</tr>
<tr>
<td>7.0</td>
<td>0.05</td>
<td>5</td>
<td>62.7</td>
<td>8 650</td>
</tr>
<tr>
<td>7.0</td>
<td>0.05</td>
<td>30</td>
<td>74.9</td>
<td>8 500</td>
</tr>
<tr>
<td>7.0</td>
<td>0.05</td>
<td>60</td>
<td>64.2</td>
<td>8 100</td>
</tr>
</tbody>
</table>
initiator concentrations and the polymerization time is shown in Table 1. When examining Figure 3 and Table 1, it is seen that the increase in the acid concentration resulted in a decrease in the molecular weight of polymer at higher Ce(IV) concentration. However, at low Ce(IV) concentration, with increasing acid concentration, the molecular weight of polymer increased. No significant change was observed in the molecular weights by extension of polymerization time. Polymerization yield remains constant at around 62–64.2% except for 74.9% of polymerization yield at 30 minutes of polymerization time. We attributed this phenomenon to an oxidation-reduction reaction between mercaptosuccinic acid and oxidant which was completed rapidly during a few minutes in the polymerization of acrylamide monomer in acid-aqueous medium. It was also observed that both colors of oxidants (Ce(IV) and KMnO₄) in polymerization reactions disappeared rapidly when their adding were completed.

To determine the acid values of PAAm with carboxyl end-groups synthesized at different initiator concentrations and at constant sulfuric acid concentration (0.10 mol/l), 0.3 g of each polymer was dissolved in distilled water and the total solution volume was 50 ml. The solutions of these polymers containing different amounts of mercaptosuccinic acid as carboxyl end-groups were titrated with 0.1 N NaOH solution by conductometric titration. The titration curves of polymer solutions containing different amounts of mercaptosuccinic acid as end-group by using 0.1 N NaOH solution as titrant were shown in Figure 6. The initial conductivities of polymer solutions, the amount of volume of 0.1 N NaOH solution at neutralization point in titration reaction and the calculated acid values of acrylamide polymers synthesized at various initiator concentrations in the polymerization reactions were given in Table 2. As can be seen from Table 2, the initial conductivities of polymer solutions and acid values of polymers indicated an increase with augmentation of mercaptosuccinic acid in different redox systems at constant sulfuric acid concentration (0.10 mol/l) in polymerization reactions. These results support the idea that polymers synthesized by using of mercaptosuccinic acid as a reducing agent in different redox systems contain carboxyl end-groups.

The UV spectrum of polyacrylamide obtained using Ce(IV)-organic acid or amino acid (with or without thiol group) redox system indicates generally a peak at 254 nm, due to the complex formation between Ce(III) ions and polymer containing reducing agent as end-groups [21–23]. Two peaks at 238 nm and 254 nm were observed in the UV spectrum of acrylamide polymer synthesized using mercaptosuccinic acid –Ce(IV) redox system (Figure 7). It was reported that similar peaks at 238 and 253 nm were obtained in the UV-Visible spectra of polyacrylamides synthesized using Ce(IV)-thioglycolic acid redox system [30]. The obtained spectrophotometric data from peak values at 238 and 254 nm in Figure 5 and the values of Ce(IV) concentrations in polymerization reactions have been listed in Table 3. As can be seen from Figure 5

Table 2. Initial conductivities of polymer solutions (0.3 g polymer/50 ml solution in distilled water) and acid values of polyacrylamides containing mercaptosuccinic acid end groups synthesized at different initiator concentrations. CAAm = 0.7 mol/l; CH₂SO₄ = 0.1 mol/l; T = 30°C; t = 10 min; nCe(IV) = nMSA

<table>
<thead>
<tr>
<th>nCe(IV)·10⁻³ [mol/l]</th>
<th>Initial conductivities of polymer solution [µS/cm]</th>
<th>VNaOH [ml]</th>
<th>nCOOH [mmol/g polymer]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>1813</td>
<td>0.62</td>
<td>0.206</td>
</tr>
<tr>
<td>14.0</td>
<td>1614</td>
<td>0.58</td>
<td>0.193</td>
</tr>
<tr>
<td>7.0</td>
<td>1305</td>
<td>0.52</td>
<td>0.173</td>
</tr>
<tr>
<td>2.8</td>
<td>1199</td>
<td>0.45</td>
<td>0.150</td>
</tr>
</tbody>
</table>
and Table 3, the decrease in the initiator concentration in the polymerization reaction led to a decrease in the absorbance values of polyacrylamide solutions (0.25 g polymer/100 ml solution in water) at 238 nm and 254 nm and the initiator concentration in polymerization reaction at 30°C. $C_{\text{AAm}} = 0.7 \text{ mol/l}; \ C_{\text{H}_2\text{SO}_4} = 0.1 \text{ mol/l}; T = 30^\circ\text{C}; t = 10 \text{ min}; n_{\text{Ce(IV)}} = n_{\text{MSA}}$

Table 3. The relation between the absorbance values of polymer solutions ($C_{\text{polmer}} = 0.25 \text{ g polymer/100 ml solution in water}$) measured at 238 nm and 254 nm and the initiator concentration in polymerization reaction at 30°C. $C_{\text{AAm}} = 0.7 \text{ mol/l}; \ C_{\text{H}_2\text{SO}_4} = 0.1 \text{ mol/l}; n_{\text{Ce(IV)}} = n_{\text{MSA}}$

<table>
<thead>
<tr>
<th>$C_{\text{Ce(IV)}} \cdot 10^3$ [mol/l]</th>
<th>Absorbance values at 254 nm</th>
<th>Absorbance values at 238 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>1.013</td>
<td>1.168</td>
</tr>
<tr>
<td>14.0</td>
<td>0.733</td>
<td>0.908</td>
</tr>
<tr>
<td>7.0</td>
<td>0.523</td>
<td>0.714</td>
</tr>
<tr>
<td>2.8</td>
<td>0.466</td>
<td>0.640</td>
</tr>
<tr>
<td>1.4</td>
<td>0.332</td>
<td>0.561</td>
</tr>
</tbody>
</table>

Figure 7. The dependence of absorbance values of polymer solution ($C_{\text{polimer}} = 0.25 \text{ g polymer/100 ml solution in water}$) on the initiator concentration in polymerization reaction. $C_{\text{Ce(IV)}} = 20 \cdot 10^{-3}(1), 14 \cdot 10^{-3}(2), 7 \cdot 10^{-3}(3), 2.8 \cdot 10^{-3}(4)$ and $1.4 \cdot 10^{-3}(5); C_{\text{AAm}} = 0.7 \text{ mol/l}; \ C_{\text{H}_2\text{SO}_4} = 0.1 \text{ mol/l}; T = 30^\circ\text{C}; t = 10 \text{ min}; n_{\text{Ce(IV)}} = n_{\text{MSA}}$

Unlike the fluorescence curve of homopolyacrylamide, the fluorescence curves of polyacrylamide obtained using mercaptosuccinic acid-Ce(IV) redox system show a peak at 351 nm (Figure 8). The peak values at 351 nm obtained from fluorescence curves of polymer solution indicated in Figure 8 and the values of different initiator concentrations in polymerization reaction were listed in Table 4. It was observed that with increasing Ce(IV) content in the polymerization reaction, the fluorescence intensity of polymer solution ($C_{\text{polimer}} = 0.25 \text{ g polymer/100 ml solution in water}$) synthesized at various initiator concentrations. $C_{\text{Ce(IV)}} = 20 \cdot 10^{-3}(1), 14 \cdot 10^{-3}(2), 7 \cdot 10^{-3}(3), 2.8 \cdot 10^{-3}(4)$ and $1.4 \cdot 10^{-3}(5); \text{excitation wavelength} = 260 \text{ nm}; \text{slit width}=1 \text{ nm}; \ C_{\text{H}_2\text{SO}_4} = 0.1 \text{ mol/l}; C_{\text{AAm}} = 0.7 \text{ mol/l}; T = 30^\circ\text{C}; t = 10 \text{ min}; n_{\text{Ce(IV)}} = n_{\text{MSA}}$

Table 4. The effect of the initiator concentration in the polymerization reaction on the fluorescence intensity of polymer solution ($C_{\text{polimer}} = 0.25 \text{ g polymer/100 ml solution in water}$; excitation wavelength = 260 nm; slit width=1 nm) at 351 nm. $C_{\text{H}_2\text{SO}_4} = 0.1 \text{ mol/l}; C_{\text{AAm}} = 0.7 \text{ mol/l}; T = 30^\circ\text{C}; t = 10 \text{ min}; n_{\text{Ce(IV)}} = n_{\text{MSA}}$

<table>
<thead>
<tr>
<th>$C_{\text{Ce(IV)}} \cdot 10^3$ [mol/l]</th>
<th>Fluorescence intensity·$10^{-4}$ at 351 nm [counts/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>15.93</td>
</tr>
<tr>
<td>14.0</td>
<td>14.24</td>
</tr>
<tr>
<td>7.0</td>
<td>11.34</td>
</tr>
<tr>
<td>2.8</td>
<td>7.56</td>
</tr>
<tr>
<td>1.4</td>
<td>7.38</td>
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</table>
observed in the FT-IR spectrum of acrylamide monomer was has been observed to shift to a band at 3450 cm$^{-1}$ in the spectrum of polyacrylamide. The characteristic C=O stretching vibration bands of amide and acid groups have been observed at 1680 and 1720 cm$^{-1}$ respectively. The peaks observed at 1620 cm$^{-1}$ which have been attributed to the –CH=CH$_2$ group observed in the FT-IR spectrum of acrylamide monomer disappeared in the FT-IR spectrum of polyacrylamide. The band at 1430 cm$^{-1}$ indicates O–H bending, the existence of C–O stretching in the plane of C–O–H bending in mercaptosuccinic acid and N–H stretching in acrylamide and polyacrylamide. There are also peaks at 1280 and 1180–1190 cm$^{-1}$ which are seen in the FT-IR spectra of acrylamide and polyacrylamide. These peaks belong to N–H stretching of amide groups in acrylamide and O–H bending respectively which are observed in the FT-IR spectra of mercaptosuccinic acid and polyacrylamide containing mercaptosuccinic acid end-groups. Moreover the peaks in the spectrum presented for polyacrylamide can arise due to metal ions absorbed in the polymer.

Potassium permanganate in spite of being a powerful and versatile oxidant is incapable of initiating vinyl polymerization by itself in dark. If, however, the polymerization medium is sufficiently acidic to dissolve the manganese dioxide produced by the interaction of vinyl monomer with permanganate, polymerization can be initiated by adding reducing agent and manganese dioxide dissolves in carboxylic or hydroxyl carboxylic acids, producing highly reactive Mn(III) ions [2, 33]. Both Mn(IV) and Mn(III) ions formed can be react with mercaptosuccinic acid to produce radicals for the polymerization of acrylamide monomer in acid-aqueous medium. The radical generation mechanism in this redox reaction occurring between Mn(III) ions and mercaptosuccinic acid can be given as in Figure 10.
As explained in the mercaptosuccinic acid-Ce(IV) redox reaction defined in this paper, the formation of free radicals given in the reaction I of Figure 10 is more probable than other reactions to initiate polymerization of acrylamide monomer, due to low S–H bonding energy. As described in previous investigations, oxidative termination of polymeric radicals is also possible by Mn(III) or Mn(IV) ions [2, 22, 30, 33–36] and polyacrylamides having chemical structures given in Figure 2 can be obtained in the polymerization of acrylamide monomer initiated with KMnO₄-mercaptosuccinic acid redox system in acid aqueous medium. Using mercaptosuccinic acid-KMnO₄ redox system, polymerization of acrylamide monomer was performed at different initiator concentrations at 30°C. It was observed that the increase of potassium permanganate concentration in polymerization reaction resulted in an increase in the yield but a decrease in molecular weight of polymer (Table 5). It is reported that manganese dioxide is produced by the interaction of vinyl monomer with permanganate and then manganese dioxide dissolves in acid producing highly reactive Mn(III) ions [2, 33]. Both Mn(IV) or Mn(III) ions reduced to Mn(II) ions during the polymerization reaction. The Mn(II) species that occur at the end of polymerization reaction are absorbed by the polymer [20–22]. The dependence of the concentration of Mn(II) which is incorporated into the polymer on the initiator concentration in the polymerization reaction is given in Figure 11. It is seen that the amount of Mn(II) bound to the polymer changes with the initial concentration of permanganate.

### 4. Conclusions

In this study, the effects of temperature, polymerization time, sulfuric acid concentration and initiator concentration on the yield and molecular weight of polymer were investigated. The results indicate that this redox system is very convenient to initiate acrylamide polymerization at room temperature. The polymerization of acrylamide using mercaptosuccinic acid-Ce(IV) or KMnO₄ redox system in acid aqueous medium was performed at room temperatures. In the polymerization of acrylamide initiated by Ce(IV)- mercaptosuccinic acid or KMnO₄-mercaptosuccinic acid redox system in acid aqueous medium, the formation radicals of –S· is energetically most favorable due to low S–H bonding energy. As a result, mercaptosuccinic acid is a convenient radical source for generation of radicals to initiate acrylamide polymerization at room temperature.

### References


